REPORT DOCUMENTATION PAGE

REPORT SECURITY CLASSIFICATION N/A		1b. RESTRICTIVE MARKINGS N/A
SECURITY CLASSIFICATION AUTHORITY N/A		3. DISTRIBUTION/AVAILABILITY OF REPORT unlimited
DECLASSIFICATION/DOWNGRADING SCHEDULE N/A		
PERFORMING ORGANIZATION REPORT NUMBER(S) 0650-520-H407		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR- 90 1170
6a. NAME OF PERFORMING ORGANIZATION Northwestern University	6b. OFFICE SYMBOL (If applicable) --	7a. NAME OF MONITORING ORGANIZATION Air Force Office of Scientific Research
6c. ADDRESS (City, State and ZIP Code) Evanston, IL 60208		7b. ADDRESS (City, State and ZIP Code) Building 410 Bolling Air Force Base, D.C. 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR	8b. OFFICE SYMBOL (If applicable) NE	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-89-0356
8c. ADDRESS (City, State and ZIP Code) Bldg 410 Bolling AFB DC 20332-6448		10 SOURCE OF FUNDING NOS.

DTIC ELECTE DEC 26 1990

	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
	61102F	2306	A1	

11. TITLE (Include Security Classification) Control of Nanostructues in Ultrahigh-Strength Steels

12. PERSONAL AUTHOR(S) Olson, Gregory B.

13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 89/7/1 TO 90/6/30	14. DATE OF REPORT (Yr., Mo., Day) 90/8/31	15. PAGE COUNT 21

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	Nanostructures, APFIM, M_2C Carbide, Nonequilibrium Composition, Interfacial Energy, Coherency Strain Energy

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The development of fine-scale multicomponent M_2C carbides in AF1410 steel was observed as a function of time at the standard tempering temperature of 510C. Strong departures from equilibrium compositions are observed at early stages of precipitation, and carbide composition appears to be particle size dependent in a given microstructure. Analysis of the carbide composition trajectory during precipitation in terms of the thermodynamic contributions of coherency and capillarity indicates initial nucleation at compositions of reduced interfacial energy but reduced chemical driving force. The ability of multicomponent carbides to follow a precipitation composition trajectory of increasing interfacial energy and increasing driving force appears important to the maintenance of a fine particle size and high number density at late stages of precipitation for overaging resistance. Preliminary evidence is also found for predicted nonuniformity of the matrix composition in the stress field of a coherent particle.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☑ SAME AS RPT. ☐ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Alan Rosenstein	22b. TELEPHONE NUMBER (Include Area Code) (202) 767-4933	22c. OFFICE SYMBOL NE

DD FORM 1473, 83 APR

EDITION OF 1 JAN 73 IS OBSOLETE.

SECURITY CLASSIFICATION OF THIS PAGE

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

CONTROL OF NANOSTRUCTURES IN ULTRAHIGH-STRENGTH STEELS

Gregory B. Olson
Materials Research Center
Northwestern University
Evanston, IL 60208

31 August 1990

Prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling Air Force Base, D.C. 20332-6448

'Summary

With the ultimate objective of establishing the principles of microstructural control to achieve efficient strengthening of ultrahigh-strength steels without embrittlement, atom-probe (AP) microanalysis was applied to the measurement of the carbide composition trajectory during precipitation of M_2C carbides in AF1410 steel. Composition was measured as a function of both tempering time and particle size, demonstrating strong departures from equilibrium for nm-scale carbides. Combining these AP results with data from coordinated electron microscopy and neutron scattering studies allowed a theoretical analysis indicating the thermodynamic contributions of capillarity and elastic coherency. The ability of multicomponent carbides to adopt a precipitation composition trajectory of increasing interfacial energy and increasing driving force appears important to the maintenance of a fine particle size and high number density at late stages of precipitation for overaging resistance. Development of quantitative thermodynamic models consistent with these new observations will play an important role in future alloy design. Preliminary evidence has also been found for predicted nonuniformity of the matrix composition in the stress field of a coherent particle, offering an important test of emerging theory of coherent thermodynamics. These results are discussed in a paper to appear in <u>Surface Science</u>, and presented at the 37th International Field Emission Symposium. Three other papers acknowledging partial AFOSR support are attached. Personnel supported in the subject grant have included Prof. G.B. Olson, Principal Investigator, Prof. T. Mori, Visiting Scientist, Dr. T.J. Kinkus, Research Associate, and C. McCarus, Research Technologist.

Accesion For	
NTIS CRA&I	☑
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and / or Special
A-1	

APFIM Study of Multicomponent M$_2$C Carbide Precipitation in AF1410 Steel

G.B.Olson, T.J. Kinkus and J.S.Montgomery

Northwestern University
Department of Materials Science and Engineering
2145 Sheridan Road, Evanston IL   60208-3116
Telephone 708-491-7826
Fax   708-491-7820

The development of fine-scale multicomponent M$_2$C carbides in AF1410 steel was observed as a function of time at the standard tempering temperature of 510° C . Strong departures from equilibrium compositions are observed at early stages of precipitation, and carbide composition appears to be particle size dependent in a given microstructure. Analysis of the carbide composition trajectory during precipitation in terms of the thermodynamic contributions of coherency and capillarity indicates initial nucleation at compositions of reduced interfacial energy but reduced chemical driving force. The ability of multicomponent carbides to follow a precipitation composition trajectory of increasing interfacial energy and increasing driving force appears important to the maintenance of a fine particle size and high number density at late stages of precipitation for overaging resistance. Preliminary evidence is also found for predicted nonuniformity of the matrix composition in the stress field of a coherent particle.

This paper was presented at the 37th International Field Emission Symposium.

Introduction

AF1410 is a high alloy Ni-Co secondary hardening martensitic steel with an exceptional combination of strength and toughness. Softening resistance during tempering is important to maintaining strength in the tough overaged structure employed in these steels, and precise control of the precipitation behavior of the nanometer-scale M_2C carbide strengthening dispersion will be necessary to design higher strength steels of this class. The high resolution microanalysis allowed by the APFIM technique is proving essential in achieving such control.

Chang and coworkers[1] first performed AP analysis on AF1410 under the standard tempering treatment of 510° C for 5hr and reported compositions for M_2C and MC carbides. Further study was undertaken to monitor the carbide sizes and compositions as a function of tempering time at 510° C by Liddle et al.[2], who observed a diminished M_2C carbon content at short tempering times. There was some indication that the presence of neon image gas suppresses the detection of carbon in the sample, but wide differences among individual particles made it difficult to characterize the effect completely. In a subsequent study on the same material, Carinci et al. [3, 4] looked more closely at the effects of operating conditions on the measured compositions. They determined that imaging gas pressures in excess of 10^{-6} mbar diminish the detection of carbon. In addition they varied the pulse ratio and determined that the measured carbon concentration saturates for pulse ratios above 20%. Sample temperature was also found to affect the analysis. Samples analyzed at 30 K tended to evaporate C_2^+ and C_3^+ clusters. At 80 K the clustering tendency diminished, at the same time reducing the overall measured carbon content. Under appropriate conditions of 22% pulse ratio and 10^{-6} mbar of neon image gas pressure, samples tempered at 510°C for 5 hr. and 8 hr. were examined and their carbide compositions measured.

In the present study we have extended observations to a wider range of tempering times, using the above prescribed operating conditions. Of particular interest for the modelling of nucleation behavior in this system is the character of the first formed particles. The AP microanalysis reported here is part of a comprehensive study of M_2C precipitation in AF1410 employing TEM and SANS described in detail elsewhere.[5].

Experimental

Samples of AF1410 of composition Fe - 14.25 Co - 10.15 Ni - 2.10 Cr - 1.05 Mo - 0.16 C were solution treated at 830°C for 1 hr., quenched, and tempered at 510°C for various times between 15 min. and 100 hr. Blanks were cut from the treated samples and specimens were electropolished according to a standard procedure [6]. A solution of perchloric acid-acetic acid (1:3) was used to thin the blanks. Polishing was then completed with a 2% solution of perchloric acid in 2-butoxyethanol [6]. Measurements were made in a VG FIM 100 atom probe with a Poschenrieder energy-compensated detector providing a mass resolution sufficient to distinguish the Ni and Co isotopes in this complex alloy. Image gas pressure was 1×10^{-6} mbar and a pulse ratio of 22% was employed. A specimen temperature of 50 K provided an optimal compromise between carbon detection efficiency and specimen failure rate. Carbides were examined by selected area probing and analyses were corrected for matrix overlap using matrix Fe,Ni, Co ratios as discussed by Chang et al. [1].

Results and Discussion

Carbide Composition Trajectory

FIM micrographs of the examined material are shown in Fig. 1. Carbides appear in bright contrast and are prominent in the 8 hr. condition of Fig. 1d. They are visible but not so prominent at earlier tempering times and indicated by arrows in Fig. 1 b-c. Small bright spots such as shown in Fig. 1a and 1b typically did not yield carbide components on analysis. Slightly larger particles produced carbide components, but only several ions per particle. Measured matrix composition in the as-quenched condition is given in Table 1. A slight reduction in Cr and Mo content relative to the alloy composition is conistent with incomplete solution treatment at the standard austenitizing temperature of 830°C. Measured carbide compositions as a function of the tempering time are indicated in Fig. 2 with $\pm 2\sigma$ confidence limits. Also shown are preliminary STEM microanalysis results for longer tempering times [5]. While carbide compositions agree with incoherent equilibrium thermodynamic predictions (cross hatched) at long times, the AP results confirm the earlier finding that the carbon site fraction is significantly diminished at short temper times, accompanied by an increase in iron. Similar effects have also been reported for AP microanalysis of M_2C precipitation in another secondary hardening steel [7]. The carbon site fraction reaches its stoichiometric value of 1.0 at 16 hr. tempering.
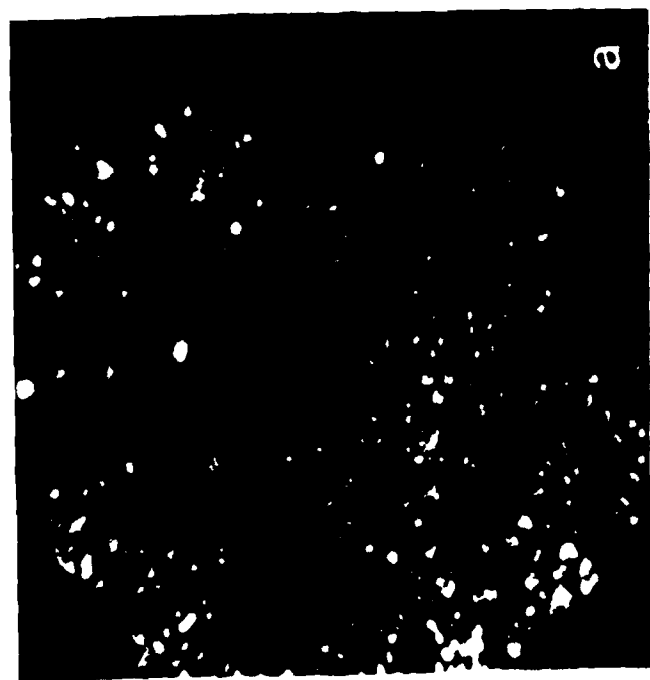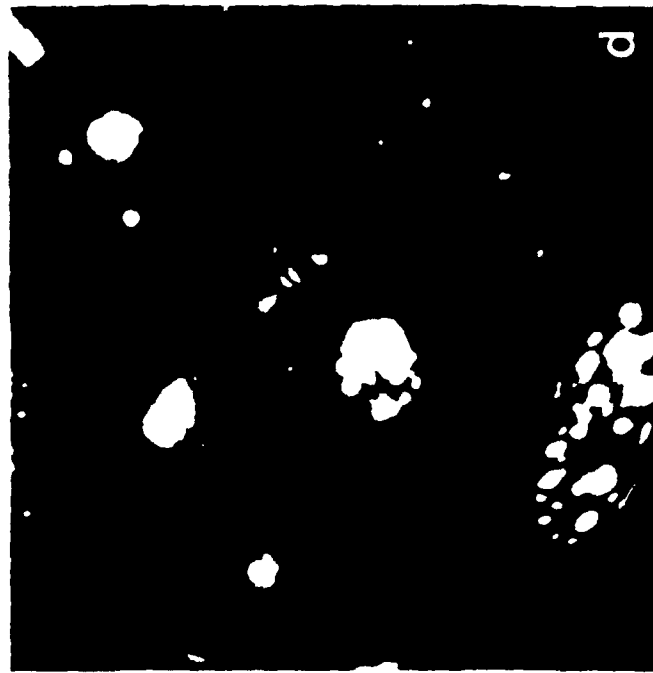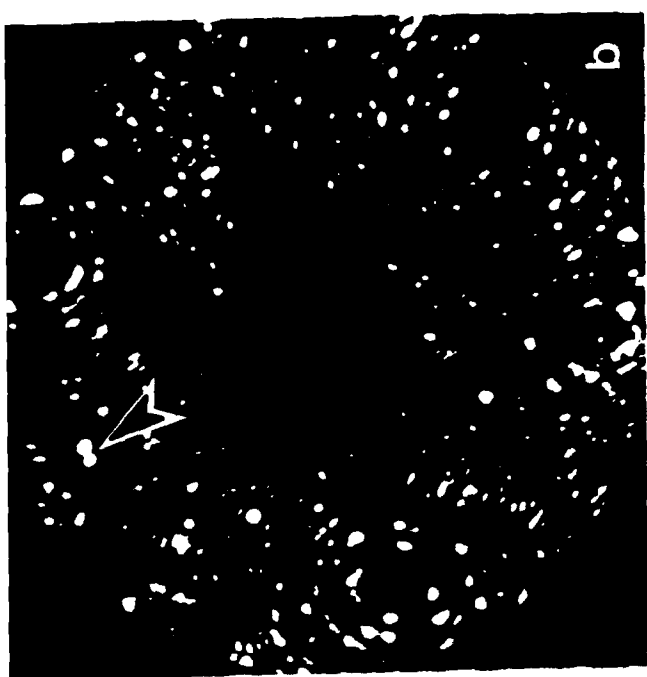
Fig. 1. FIM micrographs of AF1410 steel tempered at 510°C. [a]untempered, 8.0 kV.
[b]15min, 6.8 kV. [c]1hr, 6.4 kV. [d] 8hr, 8.3 kV.

	Measured Composition (a/o)	Nominal Composition (a/o)
C	0.056 ± 0.15	0.73
Mo	0.054 ± 0.14	0.62
Cr	1.66 ± 0.25	2.25
Ni	9.89 ± 0.59	9.75
Co	12.64 ± 0.65	13.64
Fe	74.71 ± 0.85	72.97

Table 1. Measured matrix composition of as-quenched AF1410 (830°C, 1 hr). Total number of ions collected is 10,355.

Composition of M_2C in AF1410
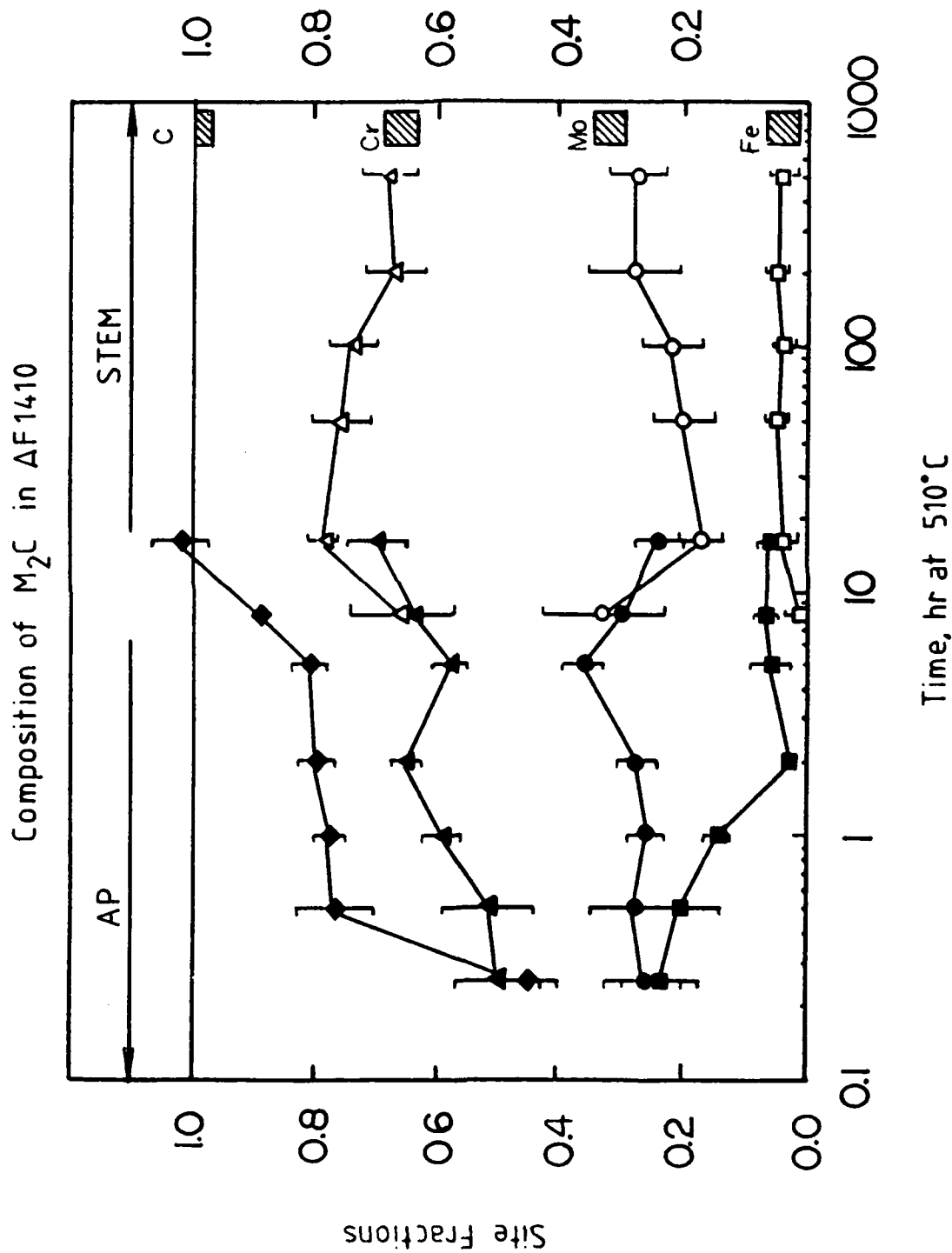
Fig 2. Measured carbide compositions as a function of tempering time at 510°C. Compositions are reported as metal and carbon site fractions.

Interpretation of the observed carbide composition trajectory has been aided by the TEM and SANS data obtained on identically heat treated samples as summarized in Fig. 3 [5]. Shown are (a) carbide particle size (determined most precisely from SANS), (b) particle shape expressed as rod aspect ratio (from TEM), (c) number density and volume fraction from SANS, (d) carbide lattice parameters from electron diffraction, and (e) alloy hardness. For the particle size figure, the solid line connects points from SANS data for which measurement errors are smaller than the symbols. The dip in the curve at 2 hr. is an indication of further nucleation, thereby reducing the average particle size[5]. The volume fraction curves verify that M_2C precipitation is nearly complete (corresponding to elimination of cementite) at the standard tempering times of 5 to 8 hr. The number density data indicate that nucleation continues over the range of 0.1 to 2 hr, beyond the half completion time, $t_{1/2}$, helping to maintain alloy hardness.

The observed downward shift of the carbide lattice parameters at shorter times is consistent with the direction of carbide composition shifts expected for particle coherency, indicative of initial precipitation in a coherent state (with coherency loss in the regime of 10 - 100 hr). An early analysis of the thermodynamics of coherent precipitation in this system indicated that coherency could account for the reduced C and increased Fe contents at early stages of precipitation [8], but recent more rigorous analysis [9,10] indicates that coherency elastic energy is accommodated primarily by adjustments in the Cr/Mo ratio.

An assessment of the composition trajectory has now been undertaken incorporating detailed calculations of particle elastic self energy and dislocation interaction energy [9] in an analysis of heterogeneous nucleation on dislocations, fit to measured nucleation rates and critical nucleus size [11]. Some results are sketched here of the analysis for which a detailed account will be presented later [12]. The size and composition of initial critical nuclei were estimated by plotting these vs. volume fraction f and extrapolating to f = 0. Critical nucleus size at 1 to 2 hr. was estimated from the particle size distributions. To define the volume chemical driving force, matrix composition was determined by mass balance. Coherency misfit strains calculated using lattice parameters consistent with these compositions were input into the elastic energy calculations [9]. Parameters thus defined are summarized in Table 2 for the stages of precipitation corresponding to tempering times of 5 min, 1 - 2 hr, and 8 hr. Two parameters were adjusted to fit observed nucleus critical size and nucleation rates, the interfacial energy γ, and an elastic self energy correction
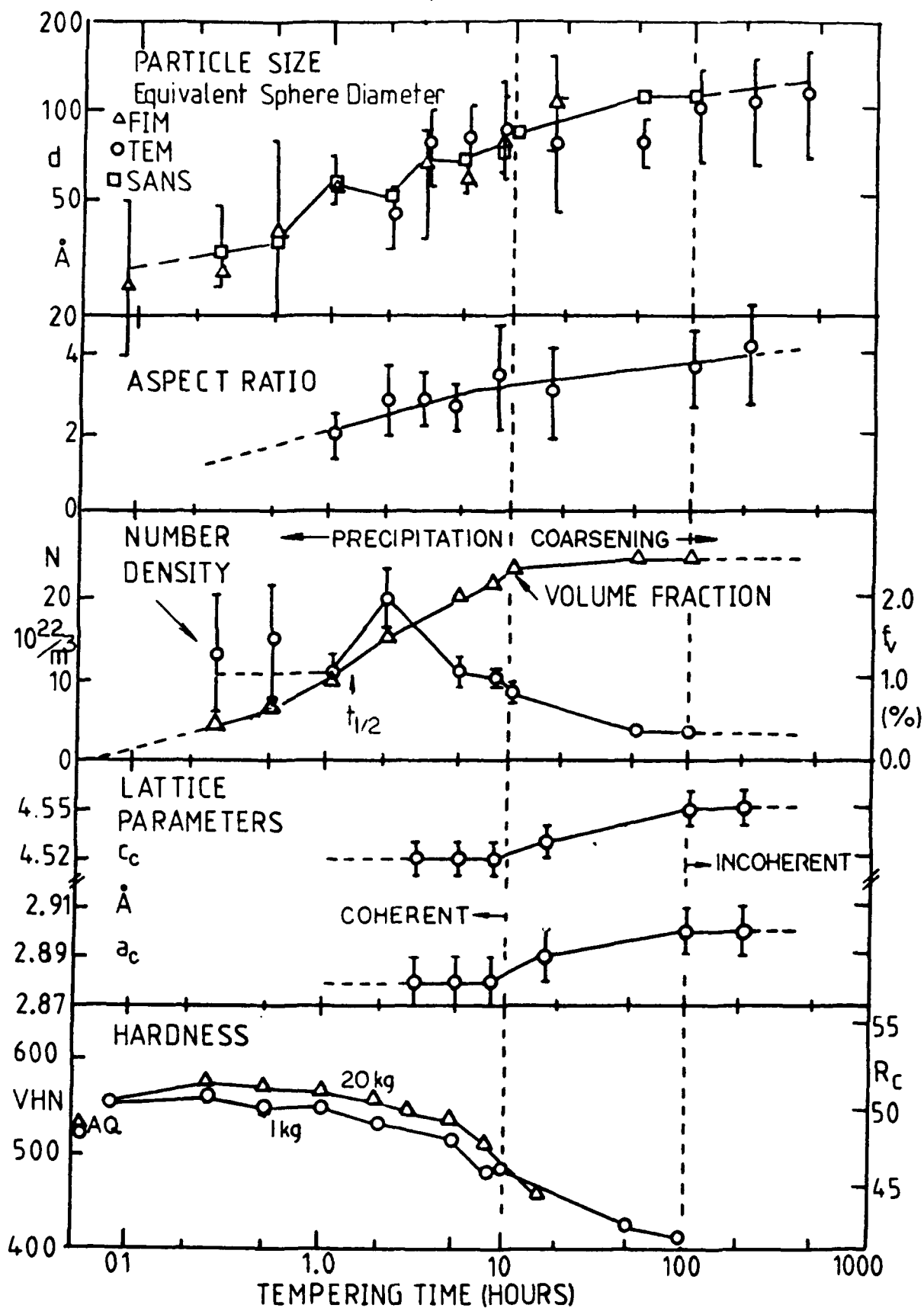
Fig. 3. M_2C carbide precipitation behavior in AF1410 steel vs. tempering time at 510°C [5].

Volume fraction M$_2$C (% theo. max)	0	59	85
Time at 510°C	5 min	1-2 hr	8 hr
M$_2$C site fraction Cr	0.47	0.59	0.64
M$_2$C site fraction Mo	0.25	0.31	0.33
M$_2$C site fraction Fe	0.28	0.10	0.03
M$_2$C site fraction C	0.62	0.81	0.89
Ferrite lattice parameter, a, Å	2.8726	2.8685	2.8690
Carbide lattice parameter, a, Å	2.8233	2.8645	2.8806
Carbide lattice parameter, c, Å	4.4586	4.5148	4.5363
Strain self energy (J/cm^3, $\alpha=1/2$)	1748	1852	1810
Driving force (J/cm^3)	-1750	-1900	-1763
Surface energy (10^{-7} J/cm^2)	99	190	

Table 2. Calculated values of nucleation parameters for M$_2$C carbides in AF1410 steel.

factor α , which adjusts down the self energy from the computed linear elastic upper bound. Best fit was obtained with α =1/2 and the γ values listed in Table 2. With α=1/2 the elastic self energy exceeds the magnitude of the chemical driving force at 8 hr tempering suggesting that particles have lost coherency at this point.

The striking result of this analysis is that the interfacial energy of the initial critical nuclei is half that of the particles forming at the last stage of nucleation (1 - 2 hr) while the precipitation chemical driving force is actually larger at 1 to 2 hr despite the reduced overall supersaturation. Our tentative interpretation is that the interfacial energy is composition dependent and is reduced by low C and high Fe in the carbide (thereby diminishing the composition difference Δc across the interface) thus attributing a major share of the observed composition trajectory effects to capillarity. The ability of multicomponent carbides to adjust composition to achieve an evolving compromise between interfacial energy and volume driving force may be an important factor in sustaining nucleation beyond precipitation half completion, enhancing the overaging resistance that is so important to the ultimate mechanical behavior of this alloy. Further research will address development of an interfacial energy model consistent with the observed composition trajectory as an aid to alloy design for greater efficiency of precipitation strengthening.

It should be noted that experimental artifacts influencing apparent Fe and C content cannot entirely be ruled out at this point, as reduced particle size might have some effect on the probing measurement. Since the carbides were examined by selected area probing, they may be partially depleted of more volatile constituents by the time they are placed under the probe hole. The associated analysis error would increase with decreasing particle size. Furthermore, an initial analysis of the fine carbides at 1/2 hr gave a reduced C site fraction of 0.5, while the higher value reported in Figure 2 was obtained after stopping down to a smaller projected aperture size. Species - dependent ion trajectory aberrations [13] may be contributing errors when the probe and particle diameters are comparable. Further analysis of the 15 min microstructure with a smaller probe diameter is underway.

Matrix Solute Distributions

The linear elastic self energy calculations discussed above employed the method of "open - system" elastic constants [14] taking into account the redistribution of matrix solutes in the stress field of the coherent carbide. The method predicts the stress and composition contours presented in Fig.4 computed for 8 hr tempering assuming full particle coherency
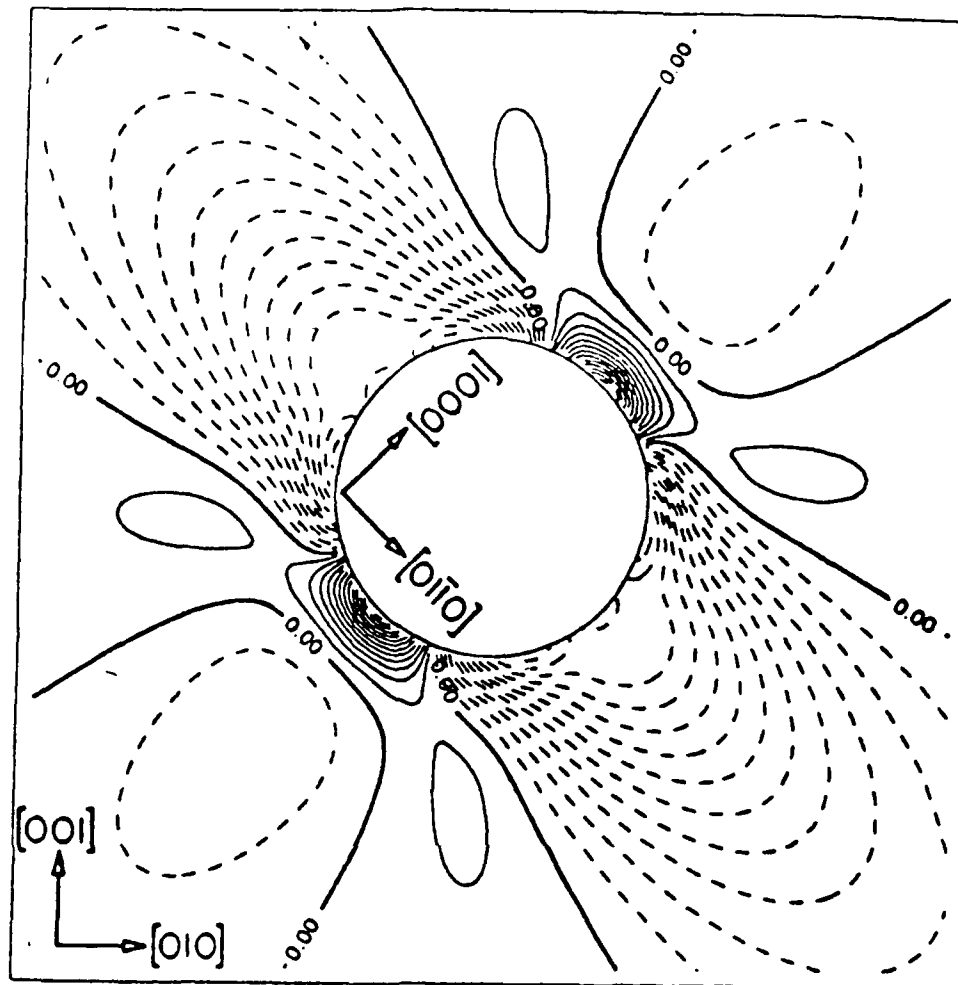
Fig. 4. Calculated stress contours in the matrix surrounding a carbide. Dashed lines indicate compressive stress and solute depletion; solid contours represent tensile stress and solute enrichment [9].

[9]. Corresponding composition profiles in planar sections are plotted in Fig 5. Solute distributions observed in an atom probe profile will clearly depend on the direction of analysis. A preliminary result obtained for the 8 hr tempered material resembling the predicted profiles in [001] type directions is presented in Fig.6. The profiles shown indicate single ion steps averaged over 30 ions. Arrows indicate average compositions of the carbide and matrix phases. Approximate location of the interface is determined by the extinction of carbon and is indicated by the dotted line. There is overlap of ion detection between carbide and matrix near the interface, so matrix elements appear simultaneously with carbide components. Local peaks in Ni and Co with possibly some Cr and Mo enhancement and associated depletion in Fe just outside the carbide resemble model predictions except that the overall Co level is low. Such enrichment was nt seen consistently, though, and the cause of solute composition variations is still open to question. If the redistribution shows no directional dependence, for example, it is more likely due to Ni-Co solute rejection from the carbide particle. Further experiments are planned to examine solute distributions in specimens with carbide orientations determined by electron microscopy, employing specimens tempered at shorter times where particles are more likely to be fully coherent. Such experiments can provide a unique test of developing theory of coherent thermodynamics.

Summary

A study of multicomponent carbide precipitation in AF1410 steel was carried out using APFIM combined with TEM and SANS techniques with the ultimate goal of controlling precipitation behavior. Departures from equilibrium compositions at short temper times reflect the roles of capillarity and coherency elastic effects. Precise composition information from APFIM together with size and volume fraction data from TEM and SANS allow thermodynamic analysis of observed nucleation behavior and the carbide composition trajectory. Such analyses so far suggest that decreased carbide C content and increased Fe content reduce the interfacial energy of initial nuclei such that the carbide composition follows a trajectory of increasing interfacial energy compensated by an increasing volume driving force. Control of such multicomponent trajectory effects to promote finer particle sizes and high number density at late stages of precipitation offers the potential for design of alloy compositions with enhanced overaging resistance. APFIM microanalysis also offers the potential for quantitative tests of theory of coherent thermodynamics essential to development of predictive theory of coherent precipitation for such alloy systems.
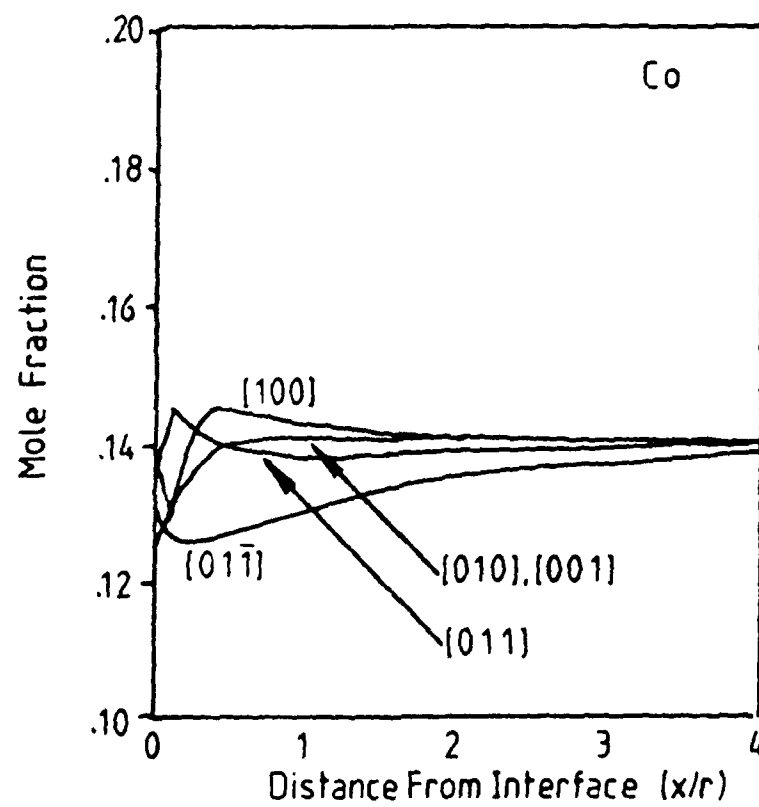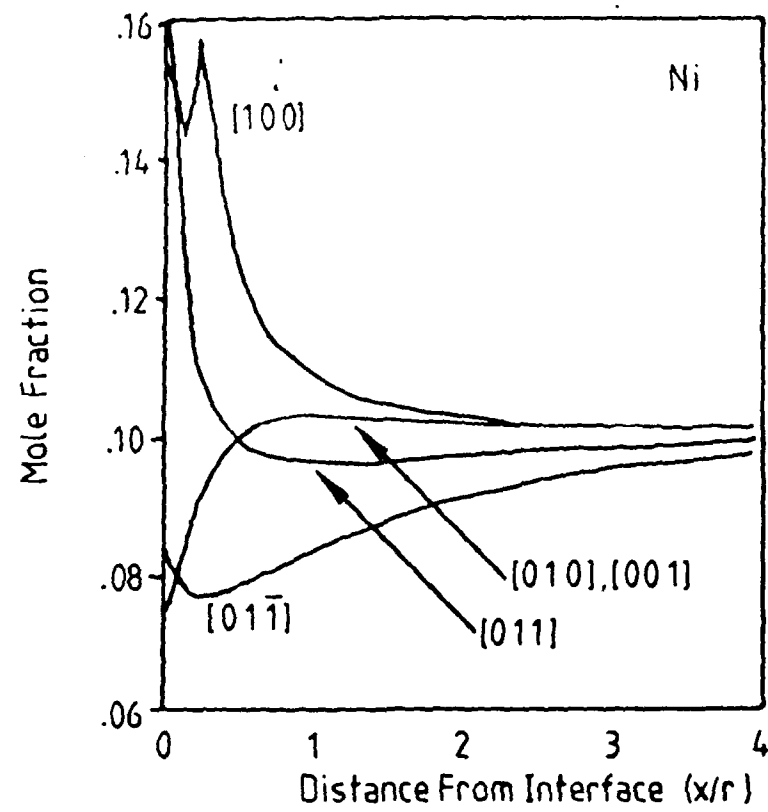
Fig. 5. Computed composition profiles in the matrix near a carbide particle[9].
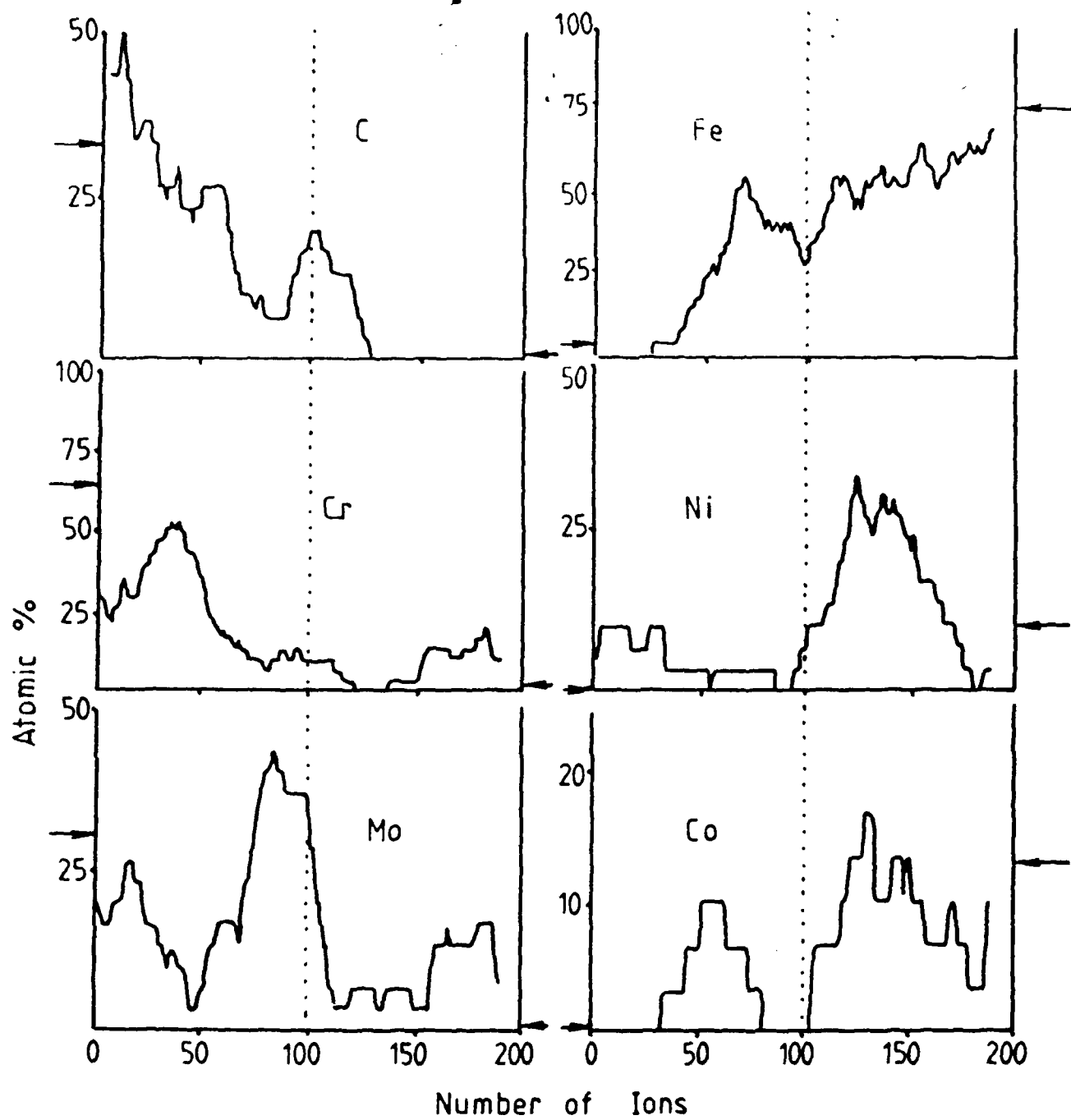
Fig. 6. Composition profile observed near carbide-matrix interface in AF1410 steel. Left arrows indicate equilibrium carbide composition values; right arrows show the matrix composition values.

Acknowledgments

References

[1] L.Chang, G.D.W.Smith and G.B.Olson, J. de Physique, 47-C2, (1985) 265.

[2] J.A.Liddle, G.D.W.Smith and G.B.Olson, J. de Physique, 47-C7, (1986) 223.

[3] G.M.Carinci, G.B.Olson, J.A.Liddle, L.Chang and G.D.W.Smith in : Innovations in Ultrahigh - Strength Steel Technology, Sagamore Army Materials Research Conference Proceedings, Vol. 34, Ed.G.B.Olson, M.Azrin and S.Wright (1990) p.179.

[4] G.M.Carinci, M.G.Hetherington and G.B.Olson, J. de Physique, 49-C6, (1988) 311.

[5] G.B.Olson, in : Innovations in Ultrahigh - Strength Steel Technology, Sagamore Army Materials Research Conference Proceedings, Vol. 34, Ed.G.B.Olson, M.Azrin and S.Wright (1990) p.3.

[6] M.K.Miller and G.D.W.Smith, Atom Probe Microanalysis: Principles and Applications to Materials Problems, (Materials Research Society , Pittsburgh, 1989), p.46.

[7] K. Stiller, L-E.Svenson, P.R.Howell, Wang Rong, H-O.Andren and G.L.Dunlop, Acta Met., 32 (1984) 1457.

[8] M.Grujicic and G.B.Olson, CALPHAD, 12 (1988) 405.

[9] K.U.C.King, Ph.D. thesis, Northwestern University, 1990.

[10] G.Ghosh and G.B.Olson, research in progress.

[11] J.S. Montgomery, "M_2C Carbide Precipitation in Co-Ni Steels", Ph.D. thesis, Northwestern University, Dec. 1990.

[12] J.S. Montgomery and G.B.Olson, manuscript in preparation.

[13] M.K.Miller, J. de Physique, 48-C6, (1987) 565

[14] F.C.Larche and J.W.Cahn, Acta metall., 33, no.3, (1985), 331.

Appendix--Size Dependence of Carbide Composition.

In the study of carbide composition as a function of tempering time, appreciable deviations from equilibrium compositions were observed as discussed in the text. These deviations were accounted for by considering contributions of capillarity and coherency elastic strain energy to the thermodynamics of precipitation. The relative importance of these terms relates to the particle sizes and thus the tempering time dependence that was observed. It was also of interest then to observe the size dependence of composition for a single tempering time.

The set of data for the 8 hr. temper treatment was reexamined for size dependence of carbide composition. Particles were separated according to the number of ions collected from each particle, as a rough measure of particle size. The result is shown in Fig. A1, with carbon and metal compositions given in M_2C site fractions. Average composition values for the 8 hr. temper are indicated by arrows on the right. Some similarities can be seen between the time dependence and size dependence. Small sized particles show a diminished carbon content as well as an enhanced iron content, corresponding to the short temper condition. The second point on the carbon figure is anomalously high, showing full site occupancy. This result may have been influenced by the presence of MC carbides, which were also observed in AF1410 steel by Chang et al.[1].

The Cr and Mo contents of M_2C carbides also show similarities between the temper time and size variations. Comparing Fig. 2 and Fig. A1-b, one notices Cr increasing and reaching a maximum as either temper time or particle size increase. The predominance of capillarity effects at small sizes is predicted to reduce Cr, while the approach to coherent equilibrium is predicted to promote a Cr increase for larger particles. In both cases, Mo is constant, then increases to a maximum, somewhat later than the Cr peak.

The data for Fig. A1 were originally recorded simply as a measurement of the average composition for the 8 hr. temper. Having seen a correspondence between the size dependence of this data set and the time dependence, it is now planned to make some further measurements of carbide composition size dependence for the single temper treatment. In these experiments, specific attention will be paid to observing the particle sizes as they are probed. A more accurate comparison of the relative sizes of particles can then be achieved. In addition, an approximate measure of the absolute sizes of particles will be recorded. The absolute size scale will be useful in correlating AP composition data with TEM and SANS data in the thermodynamic modelling process.
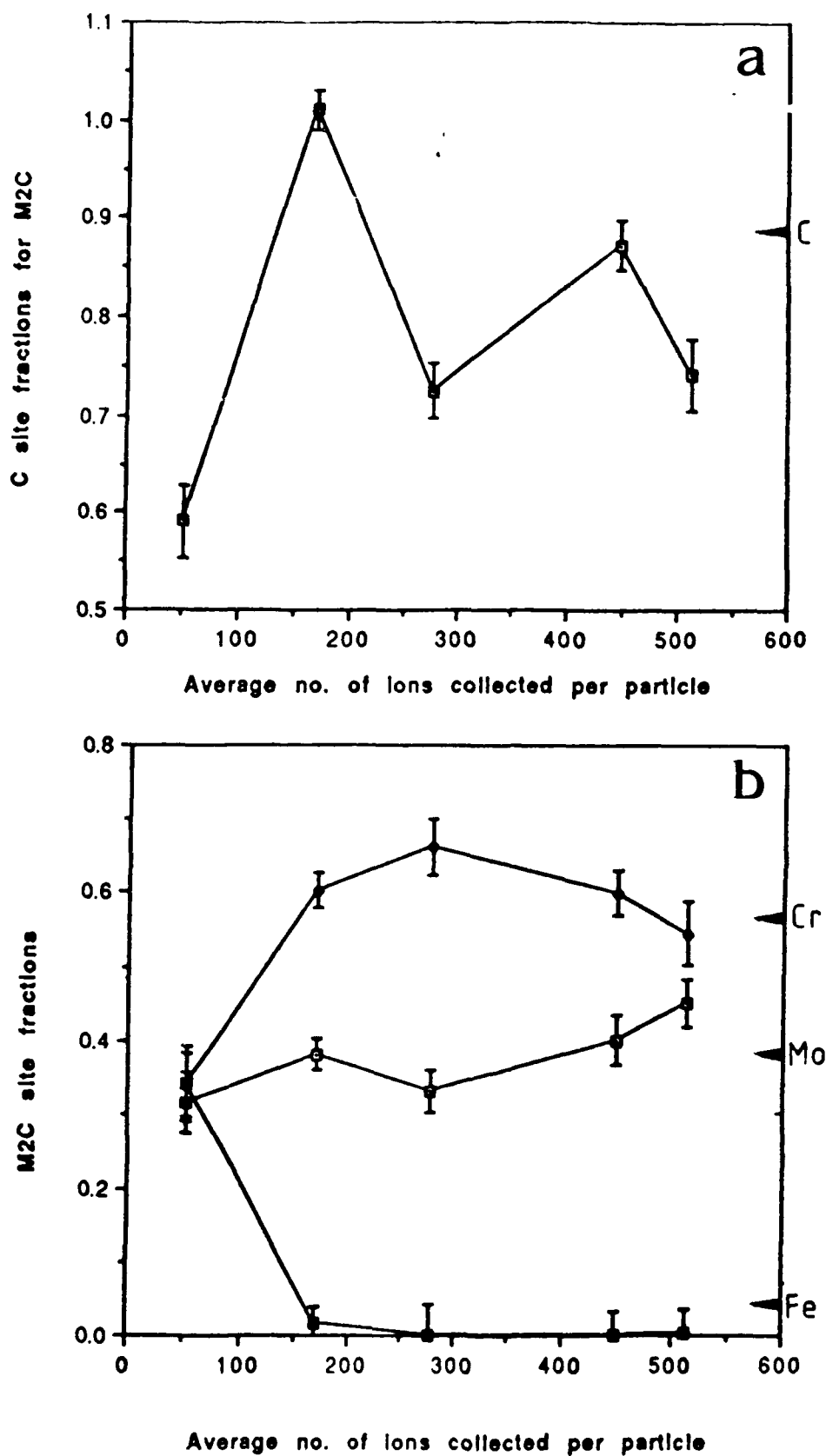
Fig. A1. (a) Carbon site fractions of M_2C carbides in the 8 hr. condition as a function of particle size. Average value is indicated by arrow on the right. (b) Site fractions of M_2C metal components as a function of time. Average values are indicated by arrows on the right.

APPENDIX

Papers Acknowledging AFOSR Support

1. "New Steels By Design," G.B. Olson, MRS Annual Meeting, Symposium XTV, Boston, MA, submitted to J. Materials Education, 1989.

2. "Materials Design: An Undergraduate Course," G.B. Olson, TMS-AIME Morris E. Fine Symposium, Detroit, MI, submitted for publication, 1990.

3. "Science of Steel," G.B. Olson, in Innovations in Ultrahigh-Strength Steel Technology, ed. G.B. Olson, M. Azrin, and E.S. Wright, Sagamore Army Materials Research Conference Proceedings: 34th (1990) p. 3.